

**A LABORATORY STUDY INVESTIGATING THE
FEASIBILITY OF APPLYING CALCITE-TYPE COATINGS
TO SEGREGATED BALLAST TANKS**

AUGUST, 1981

**Prepared by:
Ocean City Research Corporation
in cooperation with
Avondale Shipyards, Inc.**

Report Documentation Page

*Form Approved
OMB No. 0704-0188*

Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

1. REPORT DATE AUG 1981	2. REPORT TYPE N/A	3. DATES COVERED -			
4. TITLE AND SUBTITLE A Laboratory Study Investigating The Feasibility of Applying Calcite-Type Coatings to Segregated Ballast Tanks					
5a. CONTRACT NUMBER 					
5b. GRANT NUMBER 					
5c. PROGRAM ELEMENT NUMBER 					
6. AUTHOR(S) 					
5d. PROJECT NUMBER 					
5e. TASK NUMBER 					
5f. WORK UNIT NUMBER 					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Naval Surface Warfare Center CD Code 2230 - Design Integration Tools Building 192 Room 128 9500 MacArthur Bldg Bethesda, MD 20817-5700					
8. PERFORMING ORGANIZATION REPORT NUMBER 					
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) 					
10. SPONSOR/MONITOR'S ACRONYM(S) 					
11. SPONSOR/MONITOR'S REPORT NUMBER(S) 					
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release, distribution unlimited					
13. SUPPLEMENTARY NOTES 					
14. ABSTRACT 					
15. SUBJECT TERMS 					
16. SECURITY CLASSIFICATION OF: <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33%; text-align: center;">a. REPORT unclassified</td> <td style="width: 33%; text-align: center;">b. ABSTRACT unclassified</td> <td style="width: 34%; text-align: center;">c. THIS PAGE unclassified</td> </tr> </table>			a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			
17. LIMITATION OF ABSTRACT SAR	18. NUMBER OF PAGES 30	19a. NAME OF RESPONSIBLE PERSON 			

TABLE OF CONTENTS

	Page
Foreward	1
Executive Summary	2
List of Figures	3
I. Conclusions	4
II. Introduction	5
III. Background-The Development and Use of Calcite-Type Coatings	7
IV. Experimental Procedures	9
V. Results and Discussion	19
VI. Summary and Recommendations for Future Work	27
VII. References	28

FOREWARD

This research project was performed under the National Shipbuilding Research Program. Avondale Shipyards, Inc., acting on behalf of the Maritime Administration, administered the program. Mr. John Peart of Avondale Shipyards was the Technical Administrator. Mr. George Gehring of Ocean City Research Corporation was principal investigator. All of the experimental work described in this report was conducted at the Ocean City Research Laboratory in Ocean City, New Jersey.

The objective of the research study was to evaluate the feasibility of applying calcite-type coatings to segregated seawater ballast tanks. This objective relates to the overall objective of the National Shipbuilding Research Program to reduce shipbuilding costs.

EXECUTIVE SUMMARY

Much effort within the shipbuilding industry is being directed toward ways of limiting escalating coating costs. Of special concern with respect to increasing coating costs are segregated ballast tanks. The use of a calcite-type coating instead of a traditional organic-type maintenance coating represents a possible alternative approach for controlling corrosion in the segregated tanks. As a result, Avondale Shipyards acting on behalf of the Maritime Administration under the National Shipbuilding Research Program authorized the Ocean City Research Corporation to undertake a laboratory study investigating the feasibility of applying calcite-type coatings to segregated ballast tanks.

The laboratory tests indicated that deposition of uniform, adherent calcite films could be achieved fairly rapidly under flowing supersaturated solution conditions. Considering the impracticality of achieving solution flow in a ballast tank situation, the possible use of cathodic direct **current**, **a thermal gradient**, or **ultrasonic** energy to produce similar results was investigated. The results of these tests were not encouraging suggesting that further research is necessary in order to develop a suitable technique for depositing adherent, protective calcite films under quiescent conditions.

LIST OF FIGURES

FIGURE 1 Nomograph for Determination of Corrected Solubility Product for Calcium Carbonate

FIGURE 2 Nomograph for Determination of Carbonate Alkalinity

FIGURE 3 Matrix Showing Various Combinations of Conditions Included in Study

FIGURE 4 General Arrangement for Evaluating Calcite Coating Process

FIGURE 5 Appearance of Test **Specimen After \approx 72 Hours Exposure - DFI**
Index = 232 (Ref.: Test No. 3)

FIGURE 6 Appearance of Test **Specimens After \approx 24 Hours Exposure - DFI**
Index = 540 (Ref.: Tests No. 32 & 33)

FIGURE 7 Appearance of Rotating **Test Specimen After \approx 16 Hours Exposure - DFI** Index = 123 (Ref.: Test No. 37)

FIGURE 8 Appearance of Rotating **Test Specimen After \approx 16 Hours Exposure - DFI** Index = 204 (Ref.: Test No. 41)

FIGURE 9 Appearance of Rotating **Test Specimen After \approx 16 Hours Exposure - DFI** Index = 195 (Ref.: Test No. 47)

FIGURE 10 **Appearance of 3" X 6" X 1/8" Thick Steel Test Specimen After \approx 16 Hours Exposure - DFI** Index = 195, Cathodic Current = 50 ma/ft²
(Ref.: Test No. 45)

I. CONCLUSIONS

1. Under flowing conditions similar to those obtained in the subject study, uniform, adherent films of calcite can be deposited from supersaturated solution at a thickness approaching 40 microns in less than four hours.
2. Under quiescent conditions like those obtained in this study, the deposition of calcite on a steel surface will proceed at a significantly slower rate. The coating will be soft and poorly adherent, tending to deposit in a non-uniform fashion.
3. The use of direct electrical current, thermal energy, or ultrasonic energy to enhance deposition under apparently diffusion-limited, quiescent conditions does not appear promising based on the results of this study.
4. Considering the potential cost savings associated with the calcite coating approach, further research appears warranted to develop a suitable method for depositing adherent, protective calcite films under quiescent conditions.

II. INTRODUCTION

The cost of protective coating associated with the construction of a new ship has been conservatively estimated to represent approximately 15% of the total shipbuilding cost. Furthermore, it is generally believed that, in recent years, protective coating costs have been escalating more rapidly than most other shipbuilding costs. As a consequence, much effort within the shipbuilding industry is being directed toward ways of limiting the escalating coating costs.

Of special concern with respect to increasing coating costs are segregated ballast tanks. International pollution prevention regulations mandate that additional ballast volume be maintained in segregated tanks. In newer ships, the segregated ballast tanks are distributed close to the shell and bottom. The tanks are often quite narrow, with limited access. As a result, application of conventional marine coatings, like a coal-tar epoxy, becomes difficult and expensive because of the problems associated with staging, abrasive removal, and ventilation in the narrow, hard-to-reach tanks.

The use of a calcite-type coating instead of a traditional organic-type maintenance coating represents a possible alternative approach for controlling corrosion in the segregated tanks. The water works industry often relies on calcite coatings deposited from supersaturated calcium carbonate solutions as a method of corrosion control. For ballast tanks, it is envisioned that a calcite coating might be deposited on tank surfaces by flooding the tanks with a supersaturated **solution of calcium carbonate, pumped from a metering/mixing tank truck** located at dockside. The calcite coating, once deposited on the tank walls, would reduce the effective area of steel exposed to the seawater ballast. Supplementary protection would be obtained by installing sacrificial anodes in the tanks. In seawater, electrolytic current generated from the sacrificial anodes would tend to cause formation of a calcite-like film and thus reinforce and maintain the calcite coating deposited initially from supersaturated solution. It is presumed that the number of required anodes would be minimal because the initially

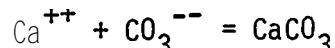
deposited calcite coating would appreciably reduce the exposed steel surface area. Potentially, the calcite coating approach offers the following advantages:

- 1) Significant reduction in surface preparation requirements. Past work suggests good adherence is obtained on reasonably clean, wire brushed surfaces.
- 2) Simpler application without major staging.
- 3) Inexpensive coating materials.
- 4) Compatible with environmental and safety regulations.
- 5) Ease of maintenance.
- 6) Substantial savings and cost.

The technique and procedures for depositing calcite coatings in the water works industry have been documented. Considering the potential advantages listed above, it appeared appropriate to conduct a study to investigate the feasibility of adapting and/or modifying the proven calcite application techniques used in the water works industry toward application to segregated ballast tanks. The following reports the results of this study.

III. BACKGROUND - - THE DEVELOPMENT AND USE OF CALCITE-TYPE COATINGS

It has long been recognized that deposition of calcite (calcium carbonate) on an immersed metal surface can provide some protection against corrosion. Deposition or precipitation of calcite from natural water proceeds according to the following reaction:



In order for calcite deposition to occur according to the above reaction, the solubility limit of calcium carbonate in the particular water must be exceeded or, in other words, the water must be supersaturated with respect to calcium carbonate.

The degree of calcium carbonate saturation in a given water depends primarily on the following factors specific to the water: (1) concentration of Ca^{++} or **calcium hardness**; (2) concentration of HCO_3^- , CO_3^{--} , OH^- or alkalinity; (3) pH; (4) total dissolved solids and (5) temperature. Quantitative indices have been developed which provide a relative measure as to the tendency of a water to precipitate calcium carbonate. The more familiar indices include the Langelier and Ryznar indices. These indices are based on equilibrium considerations with respect to the constituents listed above. However, the rate or amount of calcium carbonate that can be deposited from a given water cannot be predicted from equilibrium conditions, alone. Changes occurring near the surface of a metal (e.g. corrosion, fluid movement) can have a considerable influence on the actual deposition rate and determine whether deposition will, in fact, occur at all.

The widest use of calcite deposition as a method of corrosion control has been in the water works industry. Merrill and Sanks (1) have authored an excellent review paper. McCaulley (2) (3) & (4), in the late 1950's, conducted rather extensive studies directed at utilizing calcite deposition for internal lining and protection of cast iron water mains. McCaulley showed that dense, tenacious calcite coatings could be deposited on cast iron specimens within a few hours by appropriate control of

solution conditions. As a result of McCaul ey's work, a calcite lining process for water mains was commercialized* in the late 1960's. It is McCaul ey's work and the associated development of a commercial calcite lining process for water mains that led to the subject study. Based on a review of this work, it seemed that there was a reasonable chance that the lining process might be adapted to a segregated ballast tank ultimately resulting in a significant reduction in the cost required for corrosion control.

*Calcite Lining process - National Water Main Cleaning Co., Newark, N.J.

IV. EXPERIMENTAL PROCEDURES

The subject study used McCaul ey's work as a focal point and attempted to show on a laboratory scale that adaptation of the calcite lining process to a segregated ballast tank would be feasible. McCaul ey showed that water movement or velocity at 2-4 fps markedly enhanced the deposition rate, adhesion, and quality of the resulting calcite coating. While achievement of a relative fluid velocity of 2-4 fps is practical in the water works industry, it is difficult to envision how such fluid movement could practically be obtained for the application at hand -- that of segregated ballast tanks. However, it is also known that a cathodic direct current flowing to a surface can cause deposition of a calcite-type film. Cathodic current in segregated ballast tanks could be achieved by the installation of sacrificial anodes (zinc, aluminum, or magnesium). It was considered that the presence of a cathodic current might make up for the inability to practically achieve fluid movement in the tanks during the deposition process and result in a deposited calcite coating comparable in quality to that obtained under flowing conditions. The density of current required for optimum deposition would dictate the type, number, and arrangement of anodes in the tank. Hopefully, the required number of anodes would be significantly less than required in a non-coated tank. As a result of these considerations, the primary focus of the laboratory study was to determine if calcite coatings comparable to those reported by McCaul ey under flowing conditions could be obtained by utilizing a cathodic current instead of water velocity.

Based on McCaul ey's work and the work of others, the most important factors affecting deposition of the calcite coating are:

- 1) Water Hardness
- 2) Alkalinity
- 3) pH
- 4) Surface Condition
- 5) Cathodic Current
- 6) Dissolved Oxygen

- 7) Solution Agitation
- 8) Solution Temperature
- 9) Chemical Additives

The experimental approach pertaining to the above parameters follows:

1) Water Hardness 2) Alkalinity 3) pH

These three parameters along with temperature and total dissolved solids primarily determine the degree of calcium carbonate saturation for a given water. The combined effect of these parameters on calcite solubility is often expressed with the aid of a quantitative index like the Langelier index or Ryznar index. McCaulley derived his own index, called the DFI index, for quantitatively indicating the degree of calcite saturation of a water. In the subject experimental study, the control of hardness, alkalinity, and pH was interrelated and designed to achieve various levels of DFI index as defined by McCaulley.

The DFI index is computed as follows:

$$DFI = \frac{Ca^{++} \times CO_3^{--}}{K_c' \times 10}$$

where,

Ca^{++} = concentration of Ca^{++} (calcium hardness) as $CaCO_3$ in ppm

CO_3^{--} = concentration of CO_3^{--} (carbonate alkalinity) as $CaCO_3$ in ppm

K_c' = calcium carbonate solubility product corrected for dissolved solids and temperature.

K_s' was determined using the nomograph shown in Figure 1 taken from a standard water treatment handbook (5). The concentration of CO_3^{--} for the selected experimental conditions was determined using the nomograph shown in Figure 2. Different levels of Ca^{++} were achieved by the addition of calcium chloride (CaCl_2). Soda ash (Na_2CO_3) was used to achieve different levels of carbonate alkalinity. pH was not controlled, but was monitored throughout the tests. Calcium concentration was measured using the EDTA titrimetric method. The CO_3^{--} was experimentally measured by first determining total alkalinity using a potentiometric titration and then using the nomograph in Figure 2 to determine the concentration of CO_3^{--} .

4) Surface Condition

The results of previous work suggests that a clean, sandblasted surface is not necessary in order to form adherent calcite films. For example, Radziul et. al. (6) indicated that a "clean wire-brushed" surface was adequate to develop a good bond with the calcite coating. It would be desirable to avoid sandblasting for application to segregated ballast tanks. For the subject study, it was decided to evaluate deposition of the calcite coating under what would be considered ideal surface conditions -- clean steel surfaces with either the as-received mill finish or a sandblasted finish.

5) Cathodic Current

Since the primary thrust of the experimental study was to determine whether the application of a cathodic current in a quiescent saturated solution will result in deposited calcite coatings comparable to those obtained under flowing conditions without cathodic current, the study investigated deposition at several magnitudes of applied cathodic current: .5 ma/ft², 5 ma/ft² and 50 ma/ft². As an experimental control, deposition of calcite was also examined without an applied cathodic current.

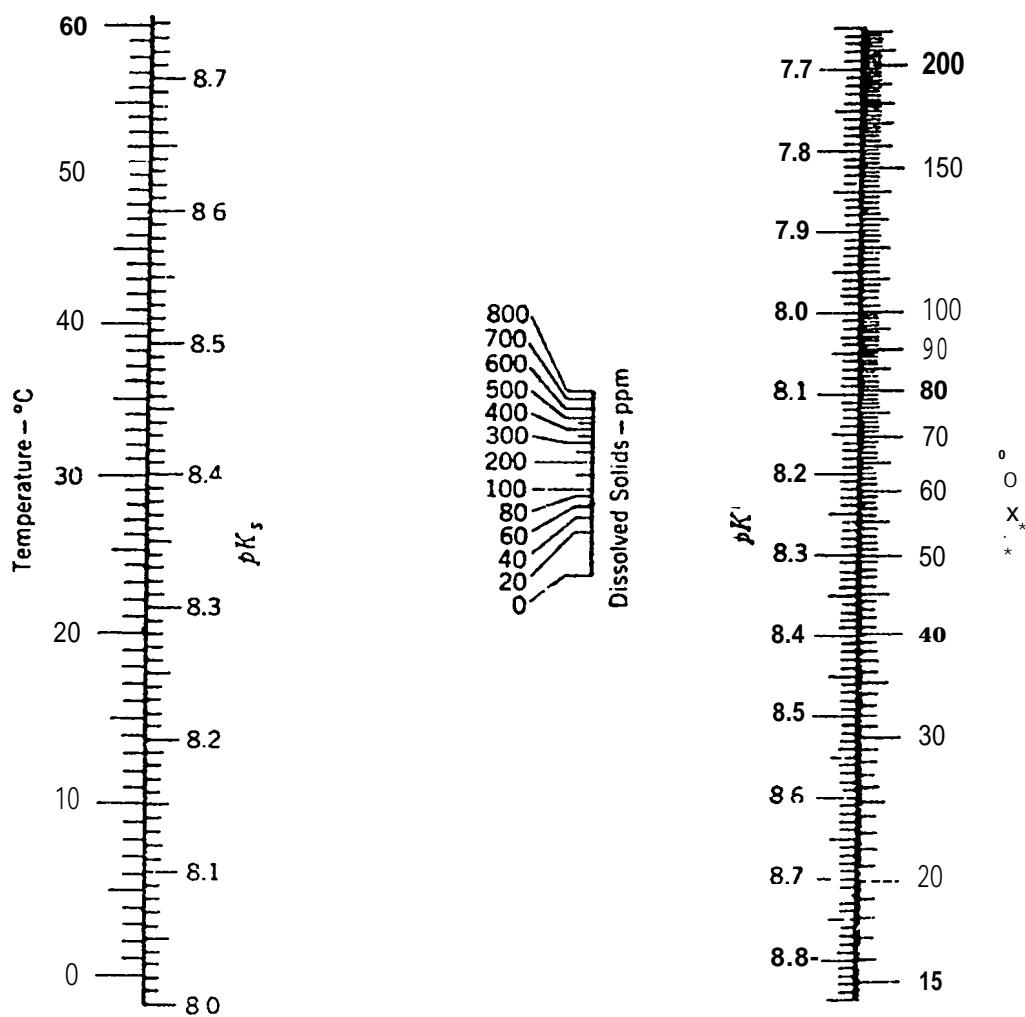


FIGURE 1 - Nomograph for Determination of Corrected Solubility Product for Calcium Carbonate

When the temperature and the concentration of dissolved solids are known, the corrected solubility product for calcium carbonate ($K_{s'}$) can be determined by extending to the scale on the right the line connecting the two known values.

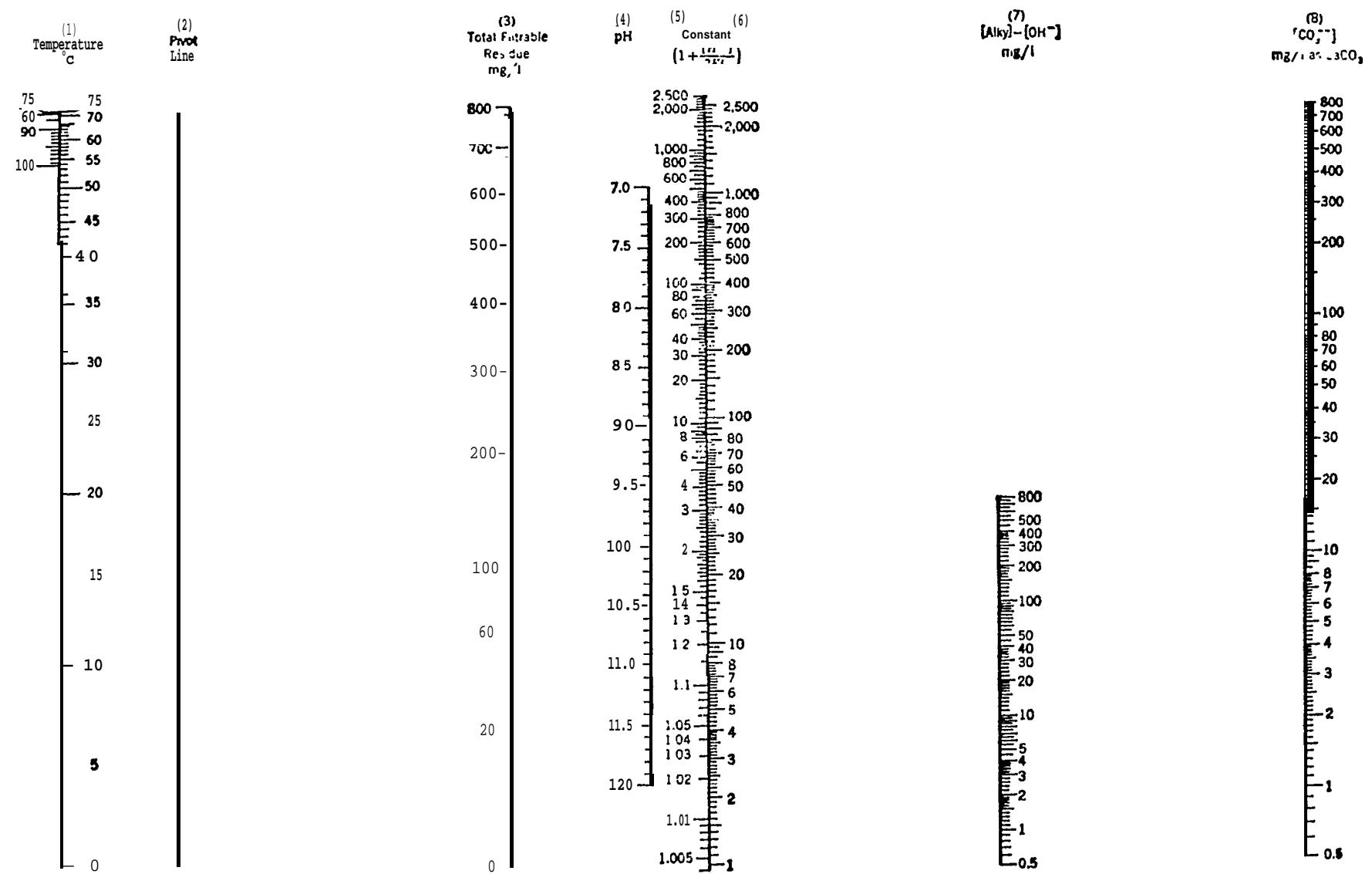


FIGURE 2 - Nomograph for Determination of Carbonate Alkalinity

(To use: align temperature (Scale 1) and total filtrable residue (Scale 3); pivot on Line 2 to proper pH (Scale 4) and read constant on Scale 5; locate constant on Scale 6 and align with nonhydroxide alkalinity on Scale 7; read carbonate alkalinity on Scale 8.)

6) Dissolved Oxygen

Stumm (7) showed that increasing the concentration of dissolved oxygen increased the rate of deposition. In practice, it would not seem difficult to achieve air-saturated conditions. Thus, air-saturated solutions were maintained for all the tests conducted in this study.

7) Solution Agitation

Although previous laboratory studies have shown that solution agitation or velocity is beneficial, in practice, it would appear to be difficult to create significant agitation in segregated ballast tanks. Thus, much of the testing in the subject program was conducted under quiescent conditions. As an experimental benchmark, some tests were also conducted under flowing or agitated conditions.

8) Solution Temperature

It is known (1) that temperature affects deposition rate. In treating shipboard ballast tanks, it would appear to be impractical to attempt to obtain solution temperatures much above ambient. Thus, testing in this study was conducted at an ambient temperature of approximately 20°C, with the exception of one series of tests discussed later.

9) Chemical Additives

In developing calcite deposition as a method of obtaining a protective lining on water mains, the addition of .5 ppm of polyphosphate to the saturated solution proved beneficial (6). As a result, the initial testing in the subject study included the injection of sodium metaphosphate at .5 ppm.

Figure 3 is a matrix summarizing the various combinations of test conditions under which calcite deposition was investigated.

FIGUIIIRE 3 - MATRIX SHOWING VARIOUS COMBINATIONS OF CONDITIONS INCLUDED IN STUDY

Test No	Calcium Hardness (as ppm CaCO_3)	Alkalinity (as ppm CaCO_3)	P ^{II}	DFI Index	Polyphosphate Injection	cathodic Current ma/ft ²	Specimen Type & Exposure Conditions
1	255	287	9.7	232	No	0	3" x 6" x 1/8", Quiescent
2	"	"	"	"	"	5	"
3	"	"	"	"	"	0	5/8" Dia. Pipe Nipple, Flowing
4	152	278	9.6	75	Yes	0	3" x 6" x 1/8", Quiescent
5	"	"	"	"	"	5	"
6	"	"	"	"	"	0	5/8" Dia. Pipe Nipple, Flowing
7	173	266	9.7	140	"	0	3" x 6" x 1/8", Quiescent
8	"	"	"	"	"	5	"
9	"	"	"	"	"	0	5/8" Dia. Pipe Nipple, Flowing
10	205	356	9.8	282	"	0	3" x 6" x 1/8", Quiescent
11	"	"	"	"	"	5	"
12	"	"	"	"	"	0	5/8" Dia. Pipe Nipple, Flowing
13	245	395	9.65	298	"	0	3" x 6" x 1/8", Quiescent
14	"	"	"	"	"	5	"
15	"	"	"	"	"	0	5/8" Dia. Pipe Nipple, Flowing
16	280	440	9.9	528	"	0	3" x 6" x 1/8", Quiescent
17	"	"	"	"	"	5	"
18	"	"	"	"	"	0	5/8" Dia. Pipe Nipple, Flowing
19	307	430	9.8	704	"	0	3" x 6" x 1/8", Quiescent
20	"	"	"	"	"	5	"
21	"	"	"	"	"	0	5/8" Dia. Pipe Nipple, Flowing
22	330	529	10.0	860	"	0	3" x 6" x 1/8", Quiescent
23	"	"	"	"	"	5	"
24	"	"	"	"	"	0	5/8" Dia. Pipe Nipple, Flowing
25	"	"	"	"	"	0	2" x 2" x 1/8", Rotating
26	375	580	10.0	969	"	0	3" x 6" x 1/8", Quiescent
27	"	"	"	"	"	5	"
28	"	"	"	"	"	0	5/8" Dia. Pipe Nipple, Flowing
29	"	"	"	"	"	0	2" x 2" x 1/8", Rotating
30	330	430	9.9	540	No	0	3" x 6" x 1/8", Quiescent
31	"	"	"	"	"	5	"
32	"	"	"	"	"	0	5/8" Dia. Pipe Nipple, Flowing

Test No.	Calcium Hardness (as ppm CaCO ₃)	Alkalinity (as ppm CaCO ₃)	pH	DFI Index	Polyphosphate Injection	Cathodic Current mA/ft ²	Specimen Type & Exposure Conditions
33	330	430	9.9	540	No	0	2" x 2" x 1/8", Rotating
34	145	269	9.8	123	"	0	3" x 6" x 1/8", Quiescent
35	"	"	"	"	"	5	" " "
36	"	"	"	"	"	0	5/8" Dia. Pipe Nipple, Flowing
37	"	"	"	"	"	0	2" x 2" x 1/8", Rotating
38	210	310	9.75	204	"	0	3" x 6" x 1/8", Quiescent
39	"	"	"	"	"	5	" " "
40	"	"	"	"	"	0	5/8" Dia. Pipe Nipple, Flowing
41	"	"	"	"	"	0	2" x 2" x 1/8", Rotating
42	190	310	9.8	195	"	0	3" x 6" x 1/8", Quiescent
43	"	"	"	"	"	.5	" " " "
44	"	"	"	"	"	5	" " " "
45	"	"	"	"	"	50	" " " "
46	"	"	"	"	"	0	5/8" Dia. Pipe Nipple, Flowing
47	"	"	"	"	"	0	2" x 2" x 1/8", Rotating
48	310	420	9.8	337	"	5	3" x 6" x 1/8", Quiescent
49	"	"	"	"	"	50	" " " "

Figure 4 shows the experimental arrangement for achieving and maintaining the selected test conditions. 3" x 6" x 1/8" steel (AISI 1010) panels were suspended in a 10 gallon glass tank. Test solutions varying in degree of calcite saturation were obtained by metering varying amounts of calcium chloride and sodium carbonate into the feedwater stream. The **make-up rate in the 10 gallon test tank was adjusted to ≈ 1 gpm in order** to keep bulk solution chemistry essentially constant. The test solution was kept air-saturated by constantly bubbling air through the solution. Electrical lead wires were attached to the test panel and a counter electrode also immersed in the test tank. The lead wires were connected to a galvanostat enabling precise control of current to the test panels.

To evaluate deposition under agitated or flowing conditions, two additional types of test specimen were included. First, a 5/8" diameter x 3" long wrought iron pipe nipple was installed in the feedwater line, downstream of the chemical injection points. The nominal flow in the line was approximately 1 fps. Secondly, a 2" x 2" x 1/8" thick steel (AISI 1018) specimen was rotated at approximately 240 rpm in the test tank. **This produced a linear velocity of ≈ 3 fps at the outer edge of the specimen.**

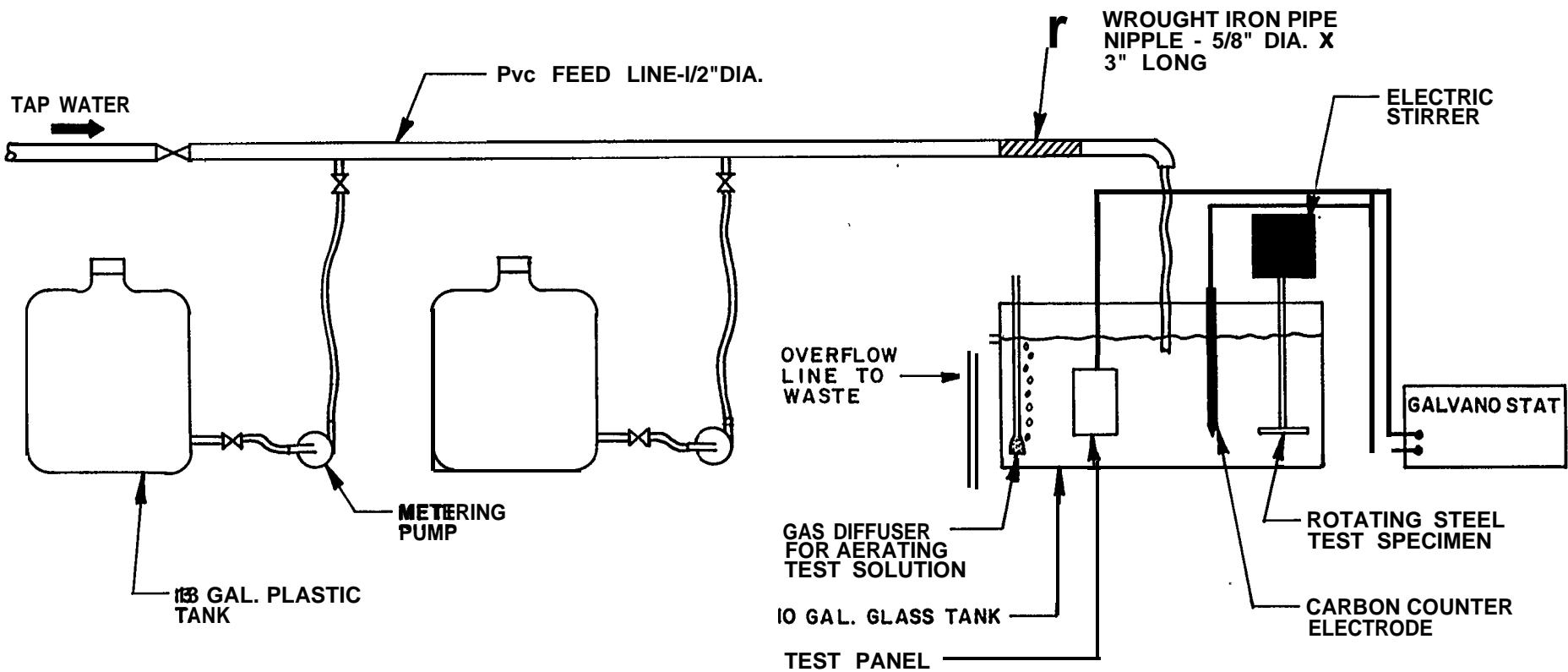


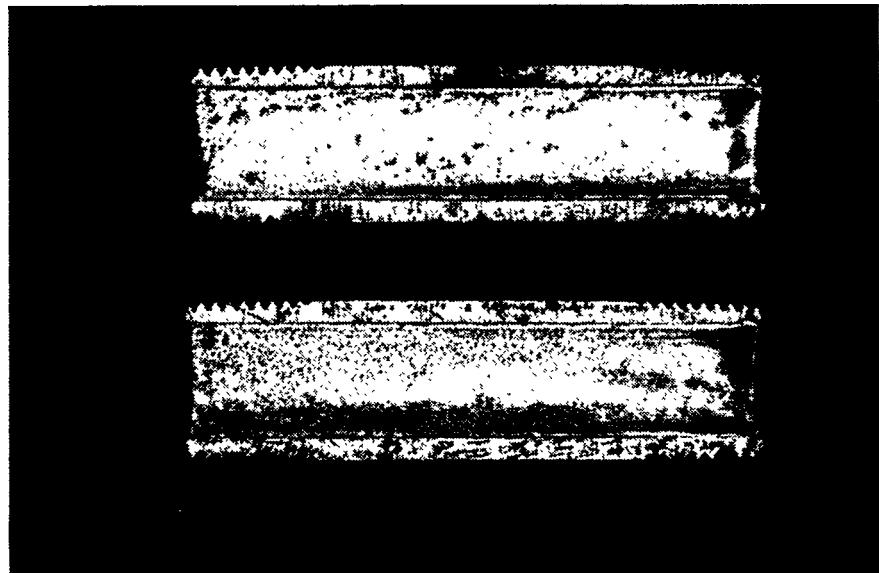
FIGURE 4 - GENERAL ARRANGEMENT FOR EVALUATING CALCITE COATING PROCESS

V. RESULTS AND DISCUSSION

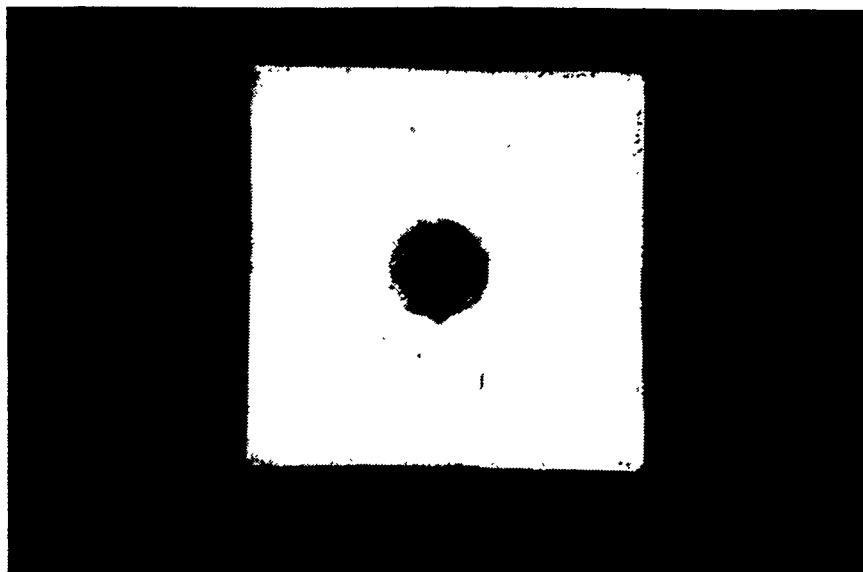
The initial tests in the study (Tests No. 1, 2 & 3 in Figure 3) were carried out under solution conditions which McCaulley suggested would yield coatings of good quality at a reasonable deposition rate (within 4 hrs.). After 72 hours exposure to saturated calcite solution conditions, no significant calcite deposition had occurred on the 3" x 6" steel specimens (Tests No. 1 & 2). The 5/8-inch diameter pipe nipple (Test No. 3) did exhibit a uniform calcite coating of approximately 20-25 roils in thickness (Figure 5). As a result, it was decided to conduct a series of additional tests where solution hardness and alkalinity would be increased incrementally, causing a corresponding increase in DFI index. For these tests, sodium metaphosphate was injected and maintained constant at a concentration of approximately .5 ppm as recommended by McCaulley. Tests No. 4 through 29 identified in Figure 3 represent this next series of tests. As observed in the initial tests, no significant calcite deposition occurred on either of the two suspended 3" x 6" specimens in any of the subsequent tests. Calcite deposition did occur on the wrought iron pipe nipple under the different solution conditions, however it tended to be spotty and thinner compared to that observed in Test No. 3, conducted without polyphosphate injection.

At this point in the study, it was decided to make two modifications in experimental procedure. First, injection of the sodium metaphosphate was discontinued. Secondly, a 2" x 2" x 1/8" rotating steel specimen was included in the test tank. After making these modifications, Tests No. 30, 31, 32, and 33 were conducted. After approximately 24 hours exposure, deposition of calcite on the rotating specimen and wrought iron pipe nipple was clearly evident (Figure 6). However, no significant deposition had occurred on the suspended steel panels. The measured thickness* of the calcite coating on the rotating steel specimen was approximately 35 roils. The coating exhibited an eggshell color similar to that described by McCaulley and had excellent adherence.

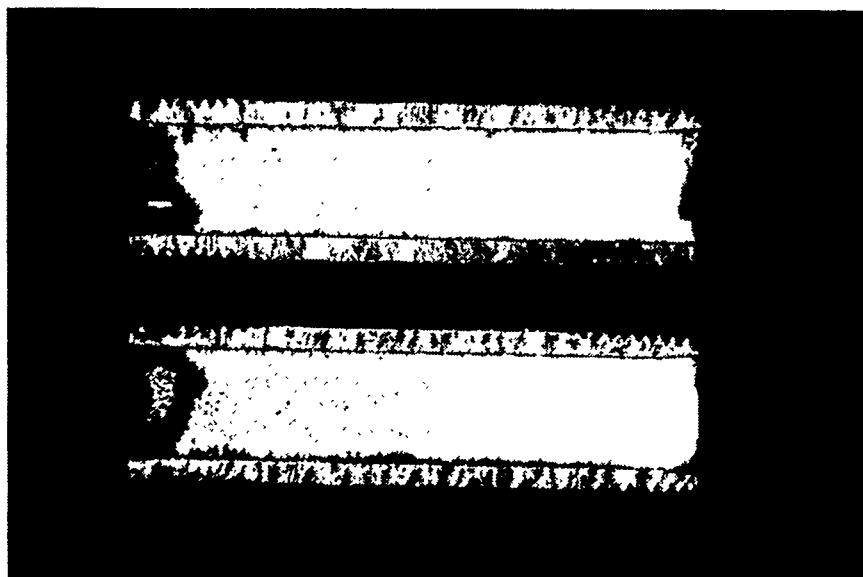
*as measured with a magnetic Mikrotest gauge



**FIGURE 5 - Appearance of Test Specimen After
≈72 Hours Exposure - DFI Index =
232 (Ref.: Test No. 3)**



a. Rotating Specimen



b. Pipe Nipple

FIGURE 6 - Appearance of Test Specimens After
≈24 Hours Exposure - DFI Index = 540
(Ref. : Tests No. 32 & 33)

Based on the results observed in Tests No. 30, 31, 32, and 33, it was decided to conduct further tests at different levels of hardness and alkalinity, without metaphosphate addition. Tests No. 34 through 42 in Figure 3 represent these tests. In these tests, calcite deposition occurred fairly rapidly (within 4 hrs.) on the rotating specimen and the wrought iron pipe nipple. Figures 7 thru 9 show the appearance of several test specimens. Again, the quality of the deposited calcite coating was good, exhibiting excellent adhesion and uniform coverage. The measured thickness ranged between 25 mils and 40 mils, depending primarily on the time of exposure to saturated solution conditions.

Deposition of calcite coating on the steel test specimens immersed under quiescent conditions, however, continued to be negligible. Application of a cathodic current at 5 ma/ft² did not result in a notable increase in calcite deposition compared to the specimen exposed without cathodic current. It did not appear beneficial to examine higher levels of supersaturation because at the last level tested significant calcite precipitation was occurring spontaneously, clogging the plastic supply line and restricting flow. Thus, higher levels don't appear practical considering the method by which a calcite coating would have to be applied in a ballast tank.

Because of the disappointing results observed on the 3" x 6" steel specimens (quiescent condition), it was decided to investigate other levels of applied cathodic current. Additional tests were carried out at cathodic currents of .5 and 50 ma/ft². 50 ma/ft² is considered to be the maximum cathodic current practical for the application at hand. The results of these tests did not show a marked change in the results reported for the previous tests. A soft, poorly-adherent non-uniform coating was observed at 50 ma/ft² (Figure 10).

Needless to say, the less-than-favorable deposition of calcite under quiescent conditions was disappointing. It had been hoped that the application of cathodic current might overcome the lack of solution agitation or flow. Previous studies investigating the calcite lining technique never established the reason for less-than-favorable calcite

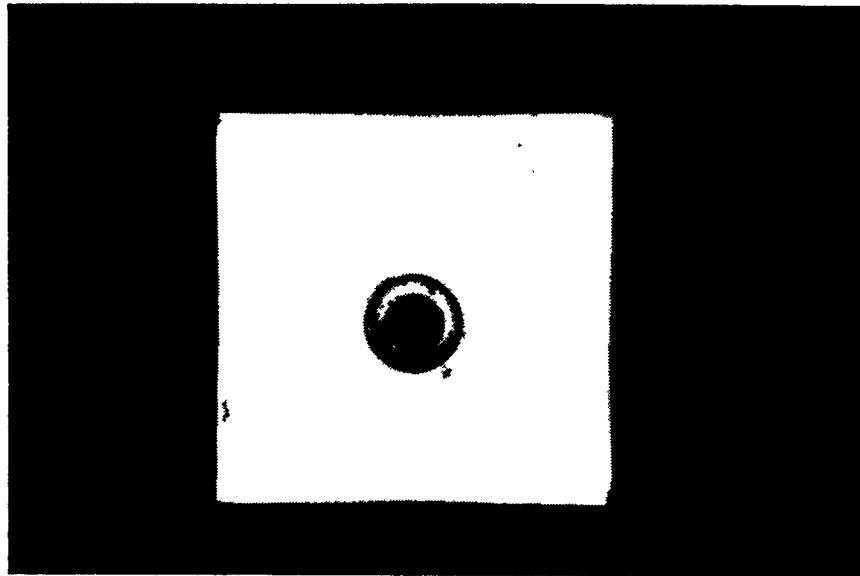


FIGURE 7 - Appearance of Rotating Test Specimen
After \approx 16 Hours Exposure - DFI Index =
123 (Ref.: Test No. 37)

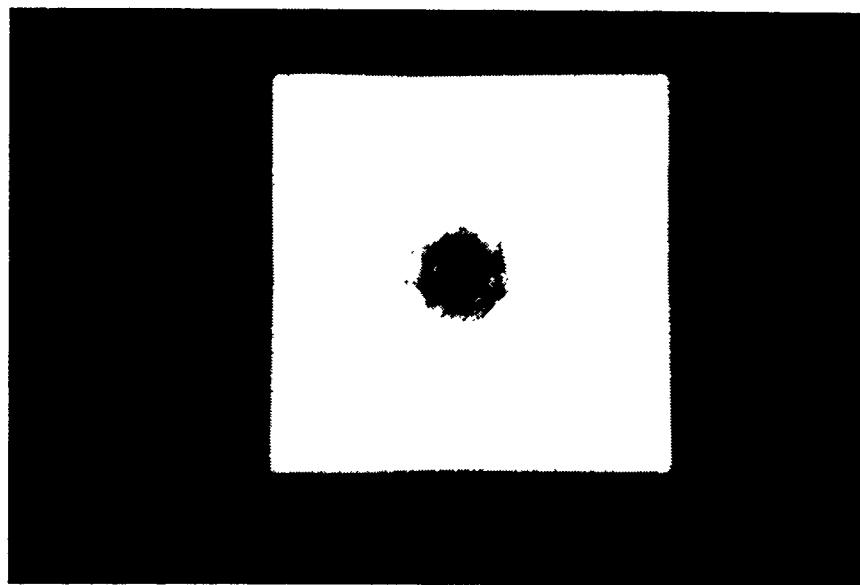


FIGURE 8 - Appearance of Rotating Test Specimen
After \approx 16 Hours Exposure - DFI Index =
204 (Ref.: Test No. 41)

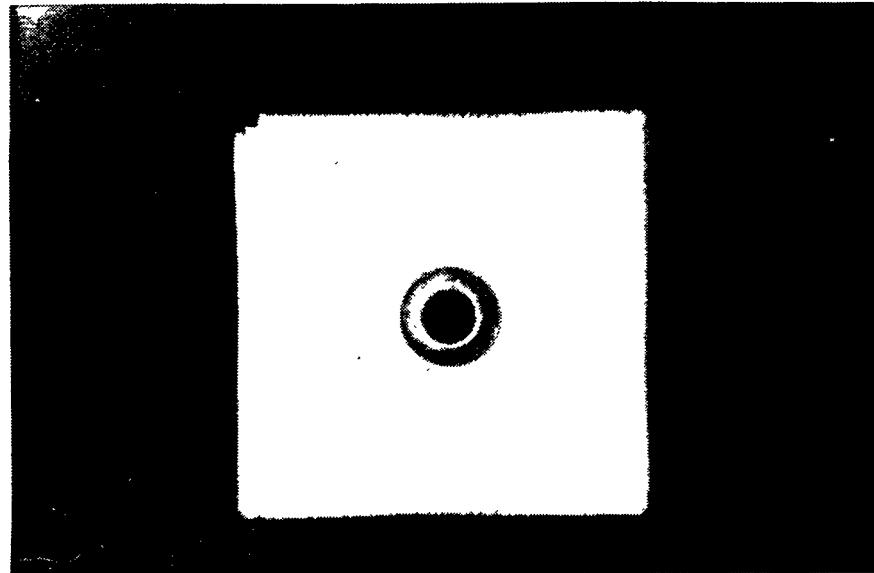


FIGURE 9 - Appearance of Rotating Test Specimen
After \approx 16 Hours Exposure - DFI Index =
195 (Ref. : Test No. 47)



FIGURE 10 - Appearance of 3" x 6" x 1/8" Thick Steel
Test Specimen After \approx 16 Hours Exposure -
DFI Index = 195, Cathodic Current = $50 \text{ ma}/\text{ft}^2$
(Ref. : Test No. 45)

deposition under quiescent conditions. Considering the results of the previous studies and the results of the subject study, it was felt that the difference in deposition characteristics under quiescent versus flowing conditions must be associated with the presence of a diffusion layer at the solution/metal interface. In other words, as calcium carbonate precipitates out of solution at the interface, the concentration of reactants (Ca^{++} & CO_3^{--}) is reduced in the solution immediately adjacent to the interface, resulting in a variation of concentration with distance from the interface toward the bulk of solution. Thus, the rate of calcite deposition is controlled by the ability of the reacting species to diffuse toward the solution/metal interface and maintain supersaturated conditions at the interface like the supersaturated conditions in the bulk solution. As has been well documented, diffusion of reacting **species** in aqueous solutions is enhanced by agitating or stirring the solution. It seems reasonable, then, that the difference in calcite deposition rate occurs because of differences in a diffusion-limited layer of solution associated with quiescent versus flowing conditions.

Considering the above-described phenomena as the possible reason for the observed differences in calcite deposition, it was thought that there might be other ways (other than fluid velocity) of changing conditions at the solution/metal interface to enhance or accelerate deposition of the calcite and at the same time be adaptable to a ballast tank situation. Two other approaches were investigated.

The first approach was to create a thermal gradient at the solution/metal interface. In a ballast tank, this might be achieved by pumping a heated supersaturated calcite solution into the ballast tanks. The tank surfaces would be at ambient temperature. To evaluate this in the lab, a test tank was divided into two separate compartments by fabricating and inserting a center wall in the tank. A 3" x 6" steel specimen was mounted in the center wall, so that each of its sides was exposed to one of the compartments. One compartment of the tank was then maintained with supersaturated

calcite solution, under conditions that yielded favorable results on a rotating specimen. The other compartment was filled with ice water to create a thermal difference between the tanks of approximately **20°C**. The results again showed limited calcite deposition on the steel specimen.

The second approach investigated as a possible way of enhancing deposition at the solution/metal interface under quiescent conditions was the use of ultrasonic energy. Although it was not readily discernible how the use of ultrasonic energy would be adapted to a ballast tank situation, it was felt that the probability of working out a practical method was great enough that a brief evaluation in the laboratory was warranted. Consequently, a steel specimen was immersed in a 700 ml ultrasonic cleaning tank through which a saturated calcite solution (DFI index 200) was pumped. No noticeable improvement in calcite deposition was obtained.

VI. SUMMARY AND RECOMMENDATIONS FOR FUTURE WORK

The laboratory tests indicated that deposition of uniform, adherent calcite films could be achieved fairly rapidly under flowing supersaturated solution conditions. Considering the impracticality of achieving solution flow in a ballast tank situation, the possible use of cathodic direct current, a thermal gradient, or ultrasonic energy to produce similar results was investigated. The results of these tests were not encouraging suggesting that another approach is required in order to produce adherent, protective calcite films under quiescent conditions.

Considering the potential cost advantages associated with the use of calcite coatings in segregated ballast tanks, it appears worthwhile to evaluate other approaches for depositing adherent, protective calcite coatings. Other approaches that seem to have some likelihood for success and should be evaluated include:

- (1) The possible adaptation or development of a spray application technique.
- (2) Other methods of disturbing the diffusion-limiting boundary layer under flooded-tank type application such as:
 - .Forced Air Agitation
 - . A.C. Current Excitation
- (3) A combination spray/flood type application
- (4) The use of chemicals additives with any of the above

VII. REFERENCES

1. D. T. **Merrill and R. L. Sanks**, Jnl. AWWA, Vol. 69, November, 1977, p. 592.
2. **R.F. McCauley**, Jnl. AWWA, Vol. 49, October, 1957, p. 1303.
3. R. F. McCaul ey and M. O. Abdul l ah, Jnl. AWWA, Vol. 50 November, 1958, p. 1419
4. R. F. McCaul ey, Jnl. AWWA, Vol. 52, November, 1960, p. 1386.
5. Standard Methods for the Examination of Water and Wastewater, 13th Edition, published by American Public Health Association, Washington, DC.
6. J. V. Radzi ul , S. J. Campbell , R. M. Brinkos, & E. J. Shervi n, Jnl. AWWA, Vol. 59, November, 1967, p. 1413.
7. W. Stumm, Jnl. AWWA, Vol. 48, March, 1956, p. 300.